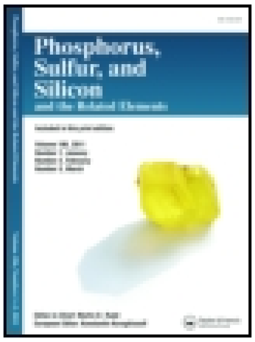

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Titanium-catalyzed hydrosilylation of olefins: A comparison study on Cp_2TiCl_2/Sm and $Cp_2TiCl_2/LiAlH_4$ catalyst system

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Abstract Hydrosilylation of olefins catalyzed by Cp_2TiCl_2/Sm (Cp = cyclopentadienyl) under solvent free conditions have been investigated. By using Cp_2TiCl_2/Sm as catalyst system, β-adducts and hydrogenation products were detected. Hydrosilylation of olefins catalyzed by $Cp_2TiCl_2/LiAlH_4$ under room temperature has also been studied. The influence of TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) on Cp_2TiCl_2/Sm and $Cp_2TiCl_2/LiAlH_4$, respectively, indicated that hydrosilylation of olefins catalyzed with Cp_2TiCl_2/Sm went through a free radical reaction pathway while a coordination mechanism was applied for $Cp_2TiCl_2/LiAlH_4$ catalyst system.

Keywords Hydrosilylation; Titanocene; Samarium; $LiAlH_4$; Mechanism; TEMPO

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1. INTRODUCTION

Hydrosilylation of olefins is a superior method for preparing alkylsilanes and other organsilicon polymers, which is particularly useful for the construction of C-Si bond [1]. Hydrosilylation of olefins was effectively promoted by transition metal complexes. Among of the metal complexes used, noble metal complexes, e.g. Karstedt's catalyst (Pt complex with 1,3-divinyltetramethyldisiloxane) and Speier's catalyst (H_2PtCl_6 in *i*-PrOH solution) often exhibit high catalytic activity. However, low selectivity of the product as well as limitation for the substrates was observed. Additionally, the high cost of these noble metal complexes also limits their application in the industry process. Hence, the development of low-cost metal catalyst systems including an iron complex [2] and a cobalt complex [3] for hydrosilylation is highly desired but remains an ongoing challenge. Although these iron or cobalt catalysts exhibit excellent catalytic activity and/or regioselectivity, these complexes exhibit one or more limitations with regard to preparation and operational convenience. The group 4 transition metal complexes, used as hydrosilylation catalysts, have been reported. Meyer *et al* [4] reported that a one-pot synthesis of functional polysilanes could be achieved through the dehydrogenative coupling of hydrosilanes and hydrosilylation reaction by using $Cp_2Ti(OPh)_2$ as catalyst. Gendre *et al* [5] reported that 1,4-hydrosilylation of dienes to allysilanes could be catalyzed by cheap and stable Cp_2TiF_2 complex, and $Cp_2TiH(SiH_2Ph)$ generated from $Cp_2TiF_2/PhSiH_3$ and regenerated from titanocene "Cp_2Ti" oxidative addition with $PhSiH_3$ as the active catalytic center was assumed, thus low-valent titanium complex plays an important role in the catalytic cycle. Silytitanocene complexes [6] and metallocene-type Ti(Ⅲ) complexes [7] were synthesized and used as catalysts for the hydrosilylation of olefins. As is well-known, low-valent organotitanium complexes play a key role in the development of both synthetic organometallic and catalytic chemistry, and among the applications of low-valent titanium in organic synthesis, the reductive coupling of carbonyl compounds to produce alkenes (the McMurry reaction) is particularly prominent [8, 9]. As a simple low-valent titanium complex system, Cp_2TiCl_2/M (M=Zn [10], Al [11], Mg [12] and Sm [13-15]) has been applied as reduction system for several organic syntheses.

The catalytic hydroalumination of olefins made it possible to synthesize organoaluminum compounds following to find new promising approaches to the synthesis of alcohols, terminal acetylenes and other functional organic compounds [16-18]. Otsuji *et al* reported that titanium-aluminium complex $Cp_2Ti(AlH_3)_2$ generated from titanocene dichloride and excess $LiAlH_4$ promoted the catalytic hydroalumination of olefins with $LiAlH_4$ to give lithium alkylhydroaluminates [19]. The study on the synthesis of organoaluminum compounds indicated that Ti and Zr complexes were usually considered as catalysts [20]. On the other hand, the hydrosilylation of olefins with monosilane in the presence of $LiAlH_4$ had been reported [21].

Here we describe the hydrosilylation of olefins can be processed with catalytic amount of Cp_2TiCl_2/M (M = Zn, Al, Mg, Fe, Co, In, Mn, Ni and Sm) or $Cp_2TiCl_2/LiAlH_4$ (Scheme 1). The comparison of these two kinds of catalyst system was studied.

[Insert Schemed 1]

2. RESULTS AND DISCUSSION

2.1 Cp_2TiCl_2/metal system for the catalytic hydrosilylation of 1-octene

In first experiments, the hydrosilylation of 1-octene with diphenylsilane catalyzed with Cp_2TiCl_2/metal as a model reaction was studied. Initially the catalytic properties of Cp_2TiCl_2, in the presence of a different metal powder for the hydrosilylation of 1-octene, were compared (Table 1). The results showed that Cp_2TiCl_2/Sm exhibit the highest catalytic activity among Cp_2TiCl_2/metals tested though all the Cp_2TiCl_2/metal tested exhibit some catalytic activity. Both β-adduct **1** and hydrogenation product **3** were obtained by using Cp_2TiCl_2/metal as catalyst, while neither α-adduct **2** nor dehydrosilylation product **4** was detected.

[Insert Table 1]

2.2 Influence of mole ratio of Cp_2TiCl_2/Sm on the catalytic hydrosilylation

Next, the influence of the mole ratio of Cp_2TiCl_2/Sm on the catalytic hydrosilylation has been investigated, and the results were summarized in Table 2. The results listed in Table 2 indicated that both the amount of catalyst and the mole ratio of Cp_2TiCl_2 /Sm have influence on the catalytic activity. The hydrosilylation reaction couldn't be conducted when only Cp_2TiCl_2 was used as catalyst (Entry 1, Table 2). Low conversion was obtained when the reaction was conducted in the presence of samarium (Entry 2, Table 2). When the amount of Cp_2TiCl_2 was 3 mol % based on 1-octene, catalytic activity was increased along with the increasing amount of samarium used from 1.5 mol % to 6 mol % (Entries 3-5, Table 2), however, further increasing the amount of samarium used resulted in the decreasing of the conversion (Entry 6, Table 2). When the amount of Cp_2TiCl_2 was 6 mol % based on 1-octene, conversion of 1-octene was decreased from 85.5 % to 65.9 % (Entry 4 *vs* Entry 7, Table 2).

[Insert Table 2]

2.3 Influence of reaction temperature on Cp_2TiCl_2/Sm catalyzed hydrosilylation

The influence of reaction temperature on hydrosilylation had been investigated, and the results were summarized in Table 3. It indicated that conversion of 1-octene increased along with the reaction temperature raising from room temperature to 120 ℃. The reaction couldn't conducted at room temperature (Entry 1, Table 3). 27.7% conversion of 1-octene was obtained at 50 ℃, and the conversion was increasing along with higher the reaction temperature. However, the best selectivity was obtained when the reaction was conducted at 100 ℃ (Entry 6, Table 3).

[Insert Table 3]

2.4 Scope of the substrates examination

By using Cp_2TiCl_2 /Sm as a catalyst, the scope of the substrates for the hydrosilylation was studied (Table 4). When Ph_2SiH_2 was used as hydrosilane, both straight chain fatty and aromatic olefins could conducted hydrosilylation reaction (Entries 1-3, Table 4), however, the addition of Ph_2SiH_2 with cyclohexene couldn't be conducted under the same conditions (Entry 4, Table 4). The steric hindrance of internal olefin should result in the lower reactive activity of cyclohexene. When $(EtO)_3SiH$ and Ph_2MeSiH was used as hydrosilane, respectively, excellent conversion of 1-octene was obtained (Entries 5-6, Table 4). No reaction occurs with Et_3SiH as hydrosilane (Entry 7, Table 4). It indicated that some silane -dependence was observed for Cp_2TiCl_2 /Sm catalyzed hydrosilylation of olefins.

[Insert Table 4]

2.5 $Cp_2TiCl_2/LiAlH_4$ catalyzed hydrosilylation of olefins

The hydrosilylation of olefins catalyzed with $Cp_2TiCl_2/LiAlH_4$ was studied (Table 5). 43.5% conversion of 1-octene was obtained by using $LiAlH_4$ (10 mol %) as catalyst at room temperature (Entry 1, Table 5). Improving the catalytic activity can be obtained by using $Cp_2TiCl_2/LiAlH_4$ as catalyst (Entries 2-7, Table 5). Among the olefins tested, both straight chain and aromatic olefins showed higher reactive for the hydrosilylation with diphenylsilane.

[Insert Table 5]

2.6 Mechanistic proposal

Related to the titanium-catalyzed hydrosilylation of olefins, two different mechanisms were proposed (Scheme 2) [1(a)]. The influence of charging sequence on the reaction had been investigated.

[Insert Scheme 2]

When the Cp_2TiCl_2/Sm was mixed with 1-octene and stirred at 100 ºC for 6 h, and then hydrosilane was added and stirred for another 6 h, no product was detected, while 71.5% conversion was obtained when the Cp_2TiCl_2/Sm was initially mixed with diphenylsilane and stirred at 100 ºC for 6 h, then 1-octene was added and continued to stirred for another 6 h. Therefore, it indicated that the formation of $[Cp_2Ti]$-SiR_3 through path (B) rather than the formation of olefin complex or alkyl complex through path (A) as the intermediate was proposed. Furthermore, the influence of TEMPO on the hydrosilylation by using Cp_2TiCl_2/Sm and $Cp_2TiCl_2/LiAlH_4$ as catalyst, respectively, had been investigated (Table 6). 76.8% conversion of 1-octene was obtained when 0.5 mol % TEMPO was added to the reaction mixtures (Entry 1, Table 6), and the reaction was completely suppressed when 3 mol % TEMPO was added (Entry 3, Table 6). In contrast, TEMPO can produce some positive effect on the hydrosilylation when $Cp_2TiCl_2/LiAlH_4$ was used as catalyst (Entries 4-6, Table 6).

Thus a free radical mechanism was proposed for Cp_2TiCl_2/Sm catalyzed hydrosilylation (Scheme 3), while coordination catalytic pathway was proposed for $Cp_2TiCl_2/LiAlH_4$ catalyzed hydrosilylation (Scheme 4). The hydrogenation products may arise from direct transfer of H from an Si-H or Ti-H moity.

[Insert Scheme 3]

[Insert Scheme 4]

[Insert Table 6]

3. CONCLUSION

The hydrosilylation of olefins can be catalyzed by Cp_2TiCl_2/metal (metal = Mg, Al, Zn, Sm, Fe, Mn, In, Co, Ni, etc.). And Cp_2TiCl_2/Sm exhibited excellent catalytic activity as well as selectivity. The hydrosilylation of olefins can also be carried out by using $Cp_2TiCl_2/LiAlH_4$ as catalyst. The difference of Cp_2TiCl_2/Sm and $Cp_2TiCl_2/LiAlH_4$ catalyst system had been examined. Though some silane -dependence was observed for both Cp_2TiCl_2 /Sm and $Cp_2TiCl_2/LiAlH_4$ catalyzed hydrosilylation of olefins, the reaction could be conducted under milder conditions by using $Cp_2TiCl_2/LiAlH_4$ as catalyst. The negative effect of TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) on the Cp_2TiCl_2/Sm catalyst system and some postive effect on the $Cp_2TiCl_2/LiAlH_4$ catalyst system, respectively, had been observed. The free radical pathway of hydrosilylation of olefins catalyzed with Cp_2TiCl_2/Sm was proposed, while the hydrosilylation of olefins through a coordination pathway by using $Cp_2TiCl_2/LiAlH_4$ as catalyst system.

4. EXPERIMENTAL

4.1 General information

Cp_2TiCl_2, zinc, aluminum, magnesium, iron, manganese, indium, cobalt, samarium, nickel powder, 1-octene, diphenylsilane, TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl), and other reagents were commercially available and were used without further purification.

Gas Chromatography: Trace DSQ GC Column = DB-5 30 m×2.5 mm×0.25 µm, split = 50:1, flow = 1 mL min^{-1} constant flow, inlet temperature = 260 ºC, column temperature = 50 ºC (hold 1 min) then 15 ºC min^{-1} up to 260 ºC (hold 10 min). The Supplemental Materials contains sample ^1H and ^{13}C NMR spectra of the known products (Figures S 1 – S 10)

4.2 General procedure for the catalytic hydrosilylation of olefins with Cp_2TiCl_2/metal

Cp_2TiCl_2 and metal powder were placed into a 10 mL round-bottomed flask equipped with a magnetic stir bar and flushed with nitrogen, and then olefin (4.0 mmol) and hydrosilane (4.4 mmol) were charged into the flask, and the resulting mixture was stirred at desired temperature for desired time. At the end of the reaction, the products were determined by GC/MS, and the conversion of alkene as well as the selectivity of products was determined by GC.

4.3 General procedure for the catalytic hydrosilylation of olefins with

$Cp_2TiCl_2/LiAlH_4$

Cp_2TiCl_2 and $LiAlH_4$ were placed into a 10 mL round-bottomed flask equipped with a magnetic stir bar and flushed with nitrogen, and then 1.0 mL diethyl ether was added, the mixture was stirred for 30 min, then olefin (4.0 mmol) and hydrosilane (4.4 mmol) were charged into the flask, and the resulting mixture was stirred at room temperature for 1 h. The products were determined by GC/MS, and the conversion of alkene as well as the selectivity of products was determined by GC.

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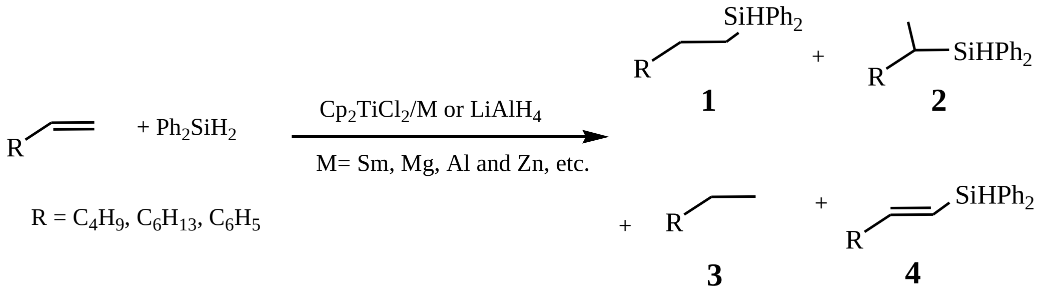
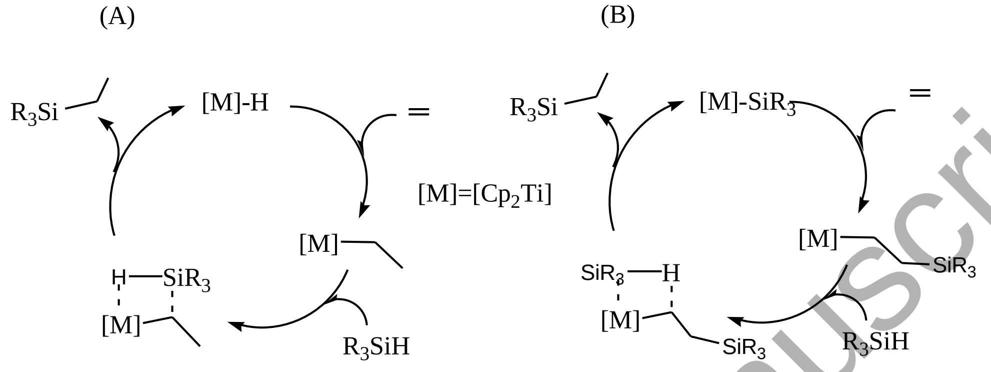
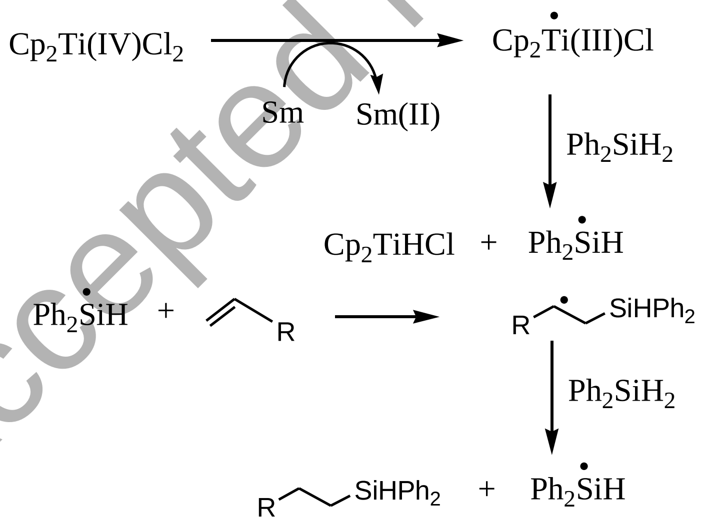


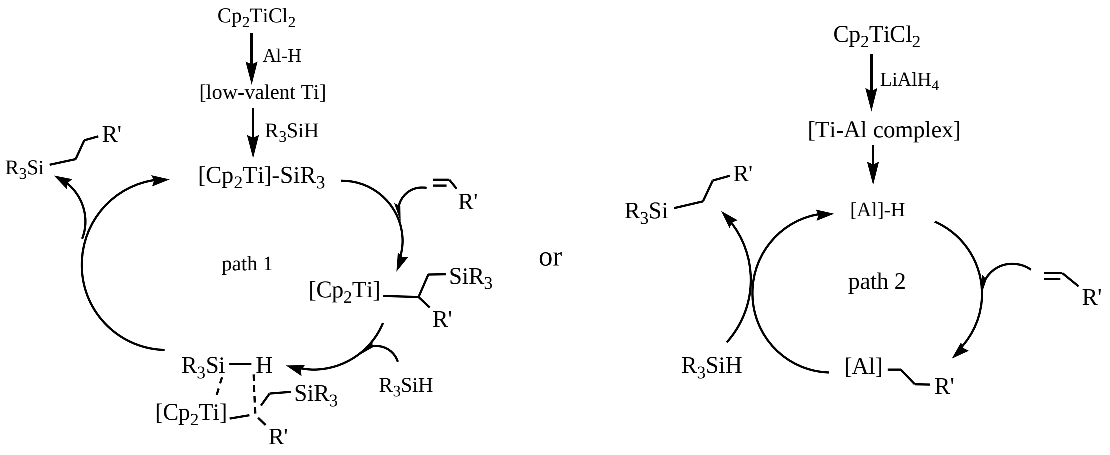
Scheme 1 Hydrosilylation of olefins catalyzed with Cp_2TiCl_2/M or $LiAlH_4$



Scheme 2 Proposed mechanism of titanium-catalyzed hydrosilylation of olefin



Scheme 3 Proposal mechanism for Cp_2TiCl_2/Sm catalyzed hydrosilylation



Scheme 4 Proposal mechanism for Cp$_2$TiCl$_2$/LiAlH$_4$ catalyzed hydrosilylation

Table 1 Hydrosilylation of 1-octene catalyzed with Cp_2TiCl_2/metal

Entry	Metal	Conv. (%)	Selectivity (%)			
			1	**2**	**3**	**4**
1	Mg	80.1	88.1	/	11.9	/
2	Al	5.4	100	/	/	/
3	Zn	57.4	67.1	/	32.9	/
4	Sm	89.0	87.6	/	12.4	/
5	Fe	65.0	83.5	/	16.5	/
6	Mn	78.9	88.5	/	11.5	/
7	In	70.5	86.0	/	14.0	/
8	Co	32.9	77.2	/	22.8	/
9	Ni	76.5	89.0	/	11.0	/

Reaction conditions: 1-octene 4.0 mmol，Ph_2SiH_2 4.4 mmol， Cp_2TiCl_2 3 mol %，Metal 6 mol %, 100 ℃，12h，

Table 2 Influence of mole ratio of Cp_2TiCl_2/Sm on the catalytic hydrosilylation

Entry	Cp_2TiCl_2(mol%)	Sm (mol%)	Conv. (%)	Selectivity(%)			
				1	**2**	**3**	**4**
1	3	/	/	/	/	/	/
2	/	3	8.2	100	/	/	/
3	3	1.5	77.7	88.4	/	11.6	/
4	3	3	85.5	87.5	/	12.5	/
5	3	6	89.0	87.6	/	12.4	/
6	3	9	88.6	86.1	/	13.9	/
7	6	3	65.9	75.1	/	24.9	/

Reaction conditions: 1-octene 4.0 mmol，Ph_2SiH_2 4.4 mmol，100 ℃，12h

Table 3 Influence of reaction temperature on Cp_2TiCl_2/Sm catalyzed hydrosilylation

Entry	Temp. (℃)	Conv. (%)	Selectivity (%)			
			1	**2**	**3**	**4**
1	rt	/	/	/	/	/
2	50	27.7	67.9	/	32.1	/
3	70	32.7	70.0	/	30.0	/
4	80	75.9	77.7	/	22.3	/
5	90	78.5	87.2	/	12.8	/
6	100	89.0	87.6	/	12.4	/
7	110	91.0	85.2	/	14.8	/
8	120	93.5	84.3	/	15.7	/

Reaction conditions: 1-octene 4.0 mmol，Ph_2SiH_2 4.4 mmol，Cp_2TiCl_2 3 mol %，Sm 6 mol %, 12h

Table 4 Substrates screened examination

Entry	Olefin	Silane	Conv. (%)	Selectivity (%)			
				1	**2**	**3**	**4**
1[a]	1-hexene	Ph_2SiH_2	96.5	89.8	/	10.2	/
2[a]	styrene	Ph_2SiH_2	100	73.5	/	26.5	/
3	1-dodecene	Ph_2SiH_2	69.0	82.5	/	17.5	/
4	cyclohexene	Ph_2SiH_2	/	/	/	/	/
5	1-octene	$(EtO)_3SiH$	76.9	41.1	/	58.9	/
6	1-octene	Ph_2MeSiH	76.8	84.1	/	15.9	/
7	1-octene	Et_3SiH	/	/	/	/	/

[a] Reaction temperature: 90 ℃

Reaction conditions: olefin 4.0 mmol，silane 4.4 mmol，Cp_2TiCl_2 3 mol %，Sm 6 mol %, 100 ℃, 12h

Table 5 Cp_2TiCl_2/$LiAlH_4$ catalyzed hydrosilylation of olefins

Entry	Cp_2TiCl_2 (mol%)	$LiAlH_4$ (mol%)	Olefin	Silane	Conv. (%)	Selectivity (%)			
						1	**2**	**3**	**4**
1	/	10	1-octene	Ph_2SiH_2	43.5	87.4	/	12.6	/
2	2	4	1-octene	Ph_2SiH_2	44.0	87.5	/	12.5	/
3	3	6	1-octene	Ph_2SiH_2	84.4	85.1	/	14.9	/
4	4	8	1-octene	Ph_2SiH_2	92.3	79.0	/	13.3	/
5	5	10	1-octene	Ph_2SiH_2	99.2	85.3	/	13.9	/
6	5	10	1-hexene	Ph_2SiH_2	100	90.6	/	9.4	/
7	5	10	1-dodecene	Ph_2SiH_2	45.7	76.4	/	23.6	/
8	5	10	styrene	Ph_2SiH_2	100	47.0	/	12.3	40.7
9	5	10	cyclohexene	Ph_2SiH_2	/	/	/	/	/
10	5	10	1-octene	Ph_2MeSiH	76.8	84.1	/	15.9	/
11	5	10	1-octene	$(EtO)_3SiH$	37.3	65.5	/	34.5	/
12	5	10	1-octene	Et_3SiH	/	/	/	/	/

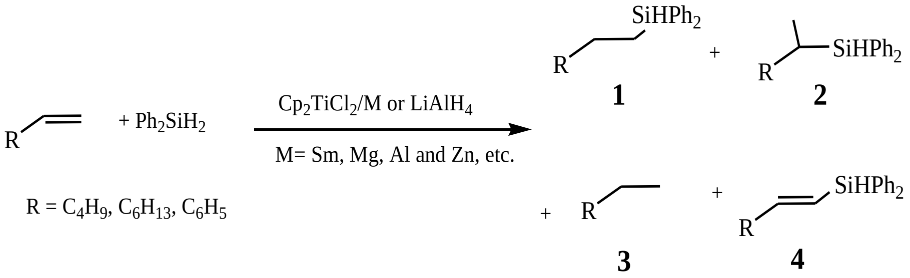
Reaction conditions: olefin 4.0 mmol，hydrosilane 4.4 mmol，Et_2O 1.0 mL, rt, 1 h

Table 6 Influence of TEMPO on the catalytic hydrosilylation

Entry	Conditions	TEMPO (mol %)	Conv. (%)	Selectivity (%)			
				1	**2**	**3**	**4**
1	Cp_2TiCl_2 3 mol %，Sm 6 mol %, 100℃,12h	0.5	76.8	84.9	/	15.1	/
2		2	73.8	85.0	/	15.0	/
3		3	/	/	/	/	/
4	Cp_2TiCl_2 5 mol %，$LiAlH_4$ 10 mol %, r.t.,1h	3	90.4	82.8	/	17.2	/
5		5	91.5	85.7	/	14.3	/
6[a]		10	97.1	88.1	/	11.9	/

Reaction conditions: 1-octene 4.0 mmol，Ph_2SiH_2 4.4 mmol，

[a] 12h.



Hydrosilylation of olefins catalyzed with Cp_2TiCl_2/M or $LiAlH_4$